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A triblock-copolymer-templating route to carbon spheres@SBA-15 large mesopore core-shell and hollow structures

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A triblock-copolymer-templating route to carbon spheres@SBA-15 large mesopore core-shell and hollow structures

Abstract

The fabrication of mesoporous core-shell and hollow spheres with ordered mesostructures and tunable large pore sizes is highly desirable for fundamental research and practical applications. A direct triblock-copolymer-templating coating approach has been provided for the synthesis of carbon sphere@mesoporous silica core-shell (CS@SBA-15) and hollow structures in an acidic medium at room temperature. These CS@SBA-15 core-shell structures possess large mesopores (6.3-8.4 nm), high surface areas (318.1-438.4 $m^2 g^{-1}$) and large pore volumes (0.31-0.36 $cm^3 g^{-1}$). The corresponding hollow mesoporous silica spheres (HMSS) with controllable mesopores (6.0-8.2 nm), high surface areas (239.9-326.5 $m^2 g^{-1}$) and pore volumes (0.37-0.62 $cm^3 g^{-1}$) can be obtained after the removal of the carbon sphere cores through calcination at 700 degrees C in air. The current research results provide an effective methodology for the synthesis of other mesoporous silica core-shell structures with large pore sizes and multilayer core-shells, and even nanorattle structures.

Keywords

copolymer, templating, route, carbon, spheres, sba, 15, triblock, large, hollow, mesopore, core, shell, structures

Disciplines

Engineering | Physical Sciences and Mathematics

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A triblock-copolymer-templating route to carbon spheres@SBA-15 large mesopore core-shell and hollow structures

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Abstract

Fabrication of mesoporeous core-shell and hollow spheres with ordered mesostructure and tunable large pore size are highly desirable for fundamental research and practical applications. A direct triblock-copolymer-templating coating approach has been provided for synthesis of carbon sphere@mesoporous silica core-shell (CS@SBA-15) and hollow structures in an acidic medium at room temperature. These CS@SBA-15 core-shell structures possess large mesopores (6.3 – 8.4 nm), high surface areas (318.1 – 438.4 m^2/g) and pore volumes (0.31 – 0.36 cm^3/g). The corresponding hollow mesoporous silica spheres (HMSS) with controllable mesopores (6.0 – 8.2 nm), high surface areas (239.9 – 326.5 m^2/g) and pore volumes (0.37 – 0.62 cm^3/g) can be obtained after removal of the carbon sphere cores through calcination at 700 ^oC under air atmosphere. The current research results provide an effective methodology for synthesis of other mesoporous silica core-shell structures with large pore size and multilayer core-shell even nanorattle structures.

Comment [HL1]: 'in air'

Keywords: carbon spheres, triblock-copolymer-templating, core-shell, hollow spheres, mesoporous silica.

1. Introduction

Recently, core-shell structures have attracted considerable interest owning to their especial nanoarchitectures, alterable compositions and sizes, which endow these materials with multifunctional properties including magnetic, electrical, optical, thermodynamics and catalytic, and thus have extensive applications in biology, physics, material science and catalysis areas.[1-4] At present, core-shell materials with differnet shell compositions such as polymer, carbon, mental, silica and mesoporous silica have been successfully synthesized.[5-9] Regarding the diverse kinds of core-shell structures, mesoporous silica coated inorganic nanomaterials have attracted great attention in reacent years because the mesoporous silica shells can serve as beginning isolated interface and easily modifiable surface, and also provide with high surface area, volume and proper accessible pore channels.[10] Until now, mesoporous silica coated core-shell structures with diversified functional cores have been reported, such as $Au@mSiO_2$,[11] $Pt@mSiO_2$,[12] $Fe_3O_4/SiO_2/Au@mSiO_2$,[13] γ-$Fe_2O_3@nSiO_2@mSiO_2$,[14] β-$NaYF_4@SiO_2@mSiO_2$,[10] carbon nanotubes@$mSiO_2$ and $SiO_2@mSiO_2$.[15,16] Moreover, these core-shell nanocomposites present excellent properties in catalysis,[12,17] adsorption,[18] druy delivery,[19] biologic imaging and photodynamic therapy.[20-22] Although much efforts has been achieved on the synthesis approaches for mesoporous silica coated core-shell structures with *n*-octadecyltrimethoxysilane (C18TMS) [23] and hexadecyltrimethylammonium bromide (CTAB) as surfactants,[17,18,20] the general pore size of the mesoporous silica shell is around 2 - 3 nm. Consequently, one of the obstacles toward practical applications is the small pore size of mesoporous silica due to the tedious synthesis methods. Therefore, the development of core-shell structures with large pore size mesoporous silica shell is necessary.[24-26]

In addition, hollow mesoporous silica spheres possessing accessible chamber, large surface area, uniform pore size, good biocompatibility and surface functionality, have revealed significant applications in many fields, e.g., adsorption, drug-delivery carriers, sensors, catalysis, etc.[27-30] Traditionally, hollow mesoporous silica spheres

Comment [HL2]: 'g'

Comment [HL3]: 'made'

are fabricated by organic soft template and sacrificial hard template. The soft template method usually requires strict control upon the reaction conditions because the soft templates such as micelles, emulsions, polymers and bubbles are sensitive to the reaction environment.[29-33] Particularly, polymer latices, carbon spheres and metal oxides can be served as hard templates with various morphologies, controllable sizes and easy removable properties.[34,35] Therefore, the hollow mesoporous silica spheres can be prepared with changeable particles sizes, tunable cavities and morphologies *via* hard template methods.

Since Li and coworkers reported a simple hydrothermal method to synthesize carbon spheres with different sizes using glucose as precursor.[36] A variety of metal oxide hollow spheres have been prepared by utilizing carbonaceous microspheres as removable template attributing to the carbon spheres with hydrophilic surface and functional groups *i.e.* OH and C=O.[37,38] Although carbon spheres have been generally applied in synthesis of all sorts of hollow structures,[39] there are lacks of reports on the synthesis of large mesopore silica encapsulating carbon spheres. Moreover, from the viewpoint of methodology, there are few reports on controllable approach to synthesis of mesoporous silica core-shell and hollow structures with large pore sizes and changeable cores by using triblock copolymers as surfactant.

Comment [HL4]: It would be better to provide reference numbers

Herein, we report a direct triblock-copolymer-templating coating strategy to synthesize the large mesopore silica coated carbon spheres core-shell structure (CS@SBA-15) and hollow mesoporous silica spheres (HMSS) by using Pluronic P123 (PEO_{20}-PPO_{70}-PEO_{20}) as a surfactant template, tetraethyl orthosilicate (TEOS) as the silica source, anhydrous magnesium sulfate as the inorganic salt in HCl solution at room temperature. These CS@SBA-15 and HMSS present ordered mesostructure, high surface area and large pore size distribution. The pore size of mesoporous silica shell can be adjusted in the range of 6.3 – 8.4 nm *via* changing the reaction conditions, including the hydrothermal temperature and the amount of anhydrous magnesium sulfate.

2. Experimental Section

2.1 Chemicals. All of chemicals were analytical grade and used without further purification. Glucose, hydrochloric acid, anhydrous magnesium sulfate, tetraethyl orthosilicate (TEOS) and hexadecyltrimethylammonium bromide (CTAB) were purchased from Sinopharm Chemical Reagent Co. (China). Triblock poly (ethylene oxide)-*b*-poly (propylene oxide)-*b*-poly (ethylene oxide) copolymer Pluronic P123 (PEO_{20}-PPO_{70}-PEO_{20}) was purchased from Acros Corp. Deionized water was used in all experiments.

2.2 Synthetic Route.

2.2.1.Preparation of carbon spheres. The carbon spheres (CS) were prepared by hydrothermal polymerization of glucose according to previous literature method.[36] Briefly, 2.73 g of glucose was dissolved in 25 mL of deionized water and stirred for 20 minutes to form a clear solution. Subsequently, the solution was transferred into a 30 mL of Teflon-sealed autoclave for hydrothermal treatment at 180 °C for 8 h. The black samples were obtained by continuously centrifugation at 5000 rpm for 5 min and washed with water and ethanol, respectively. The finial products were obtained after vacuum-drying at 40 °C for 12 h.

2.2.2. Synthesis of CS@SBA-15 and hollow mesoporous silica spheres. CS@SBA-15 core-shell structures were synthesized using nonionic copolymer as a surfactant and TEOS as the silica source in acidic medium. In a typical procedure, 0.06 g of P123 and 0.18 g of anhydrous magnesium sulfate were all dissolved in 30 mL of 2 M hydrochloric acid. Then, 0.15 g of carbon spheres was added into the above transparent solution under ultrasonic treating for 30 min. Finally, 0.15 g of TEOS was added dropwise to the mixture and stirred for 24 h before being transferred to an autoclave and heated at 100 °C for 24 h. The precipitate was obtained by centrifugation and washed with water and ethanol for three cycles. Then the black powder was dried in vacuum-oven at 40 °C for more than 6 h. The large mesopore silica coated carbon sphere samples (CS@SBA-15) were obtained after calcination at 350°C for 5 h under nitrogen atmosphere with the heating rate of 1°C/min. The carbon sphere core was removed at 700 °C for 3 h under air atmosphere, and then the hollow mesoporous silica spheres with large pore size (HMSS) were formed. The

Comment [HL5]: 'in air'

CS@SBA-15 100H and HMSS 100 H were prepared with the hydrothermal treatment at 100 °C for 24 h without addition of the anhydrous magnesium sulfate. The CS@SBA-15 130H-$MgSO_4$ and HMSS 130H-$MgSO_4$ were synthesized with anhydrous magnesium sulfate as inorganic salt and hydrothermal treatment at 130 °C for 24 h. The traditional mesoporous silica hollow spheres were obtained by using carbon spheres as a core, CTAB as the surfactant, TEOS as the silica sources in ammonia/ethanol/water solution and calcination at 700 °C under air atmospheres.

Comment [HL6]: 'in air'

2.3 Characterization. Scanning electron microscopic (SEM) images were obtained on a Philip XL30 microscope. A thin film of gold was sprayed on the sample before characterization. Transmission electron microscopy (TEM) measurements were achieved on a JEOL 2011 microscope operated at 200 kV. The samples were suspended in ethanol and dried on a holey carbon film on a Cu grid for TEM measurements. Nitrogen sorption isotherms were measured at 77 K with a Micromeritcs Tristar 3020 analyzer (USA). Before measurements, the samples were degassed in a vacuum at 180 °C for at least 6 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas (S_{BET}), using adsorption data in a relative pressure range from 0.04 to 0.2. The pore volume and pore size distributions were derived from the adsorption branches of isotherms by using Barrett-Joyner- Halenda (BJH) model. The total pore volume V_t, was estimated from the amount adsorbed at a relative pressure P/P_0 of 0.995. Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D4 X-ray diffractometer (Germany) with Ni-filtered Cu Kα radiation (40 kV, 40 mA).

3. Results and Discussion

The large mesopore silica coated carbon spheres core-shell structure (CS@SBA-15) and the corresponding hollow mesoporous silica spheres (HMSS) are fabricated *via* three steps. As described in Scheme 1, first, carbon spheres are prepared as the core. Then, the large mesopore silica is coated on the surface of carbon spheres by using Pluronic P123 as surfactant template under an acidic system. Sequentially, the removal of surfactant P123 and carbon sphere core to obtain CS@SBA-15 and HMSS,

Comment [HL7]: 'with core'

respectively.

The carbon spheres are prepared with a hydrothermal method by using glucose as the carbon species. Fig. 1A displays a typical scanning electron microscopy (SEM) image of carbon spheres with average diameter of about 550 – 650 nm. These uniform spheres with smooth surface possess hydrophilic property and can resist the etching under strong acid system, therefore the carbon spheres can interact with triblock copolymer P123 and silica source TEOS in acidic medium. After calcined the as-made samples under nitrogen atmosphere at 350 °C to remove the triblock copolymer surfactant, the CS@SBA-15 core-shell structure isare obtained. As shown in Fig. 1B, the CS@SBA-15 products are all spherical in large-scale, indicating the uniform coating process. Interestingly, the surface of these spherical samples become rough and tend to aggregation, as well as some strip-like structure can be observed, revealing the successful coating of mesoporous silica. The morphology and microstructure of the obtained CS@SBA-15 are further characterized by transmission electron microscopy (TEM). The TEM image shows the carbon spheres have been all coated by homogeneous mesoporous silica with the thickness of 120 – 150 nm (Fig. 2A). The magnification TEM image further reveals the typical core-shell structure. Additionally, the shell is composed of tens of mesopore channels with the pore size of 6.5 nm and wall thickness of about 6 nm (Fig. 2B). It is noteworthy that the mesoporous silica shell displays parallel mesoporous regional trend and some stripe-like mesochannels in the [110] direction, demonstrating a 2-D hexagonal ordered mesostructures (Fig. 2B). This result is well agreement with the typical TEM images of SBA-15 mesoporous silica reported elsewhere.[42]

Comment [HL8]: 'sintering'

The small-angle X-ray diffraction (XRD) pattern for CS@SBA-15 shows an obvious diffraction peak at $2\theta = 0.86^{o}$ that is indexed as (100) reflection associated with *p6mm* hexagonal symmetry (Fig. 1D), indicating an ordered mesostructures. N_2 sorption isotherms of the CS@SBA-15 (Fig. 3A) presents a typical type IV curves with capillary condensation step at broad relative pressure (P/P_o) of 0.5 - 0.7, suggesting the uniform large pore size. The hysteresis loops are classified to H1-type, assigned to the narrow pore size distribution and 1D cylindrical channels. The pore

size calculated using Barrett-Joyner-Halenda (BJH) analysis with adsorption branch, shows a narrow distribution at 6.7 nm (Fig. 3B). This result agrees very well with the TEM images (Fig. 2 A and 2B). Moreover, the CS@SBA-15 core-shell structure has a high BET surface area of 438.4 $m^2 g^{-1}$ and large pore volume of 0.36 $cm^3 g^{-1}$ (Table 1).

Since the triblock copolymer surfactant and carbon spheres can be easily removed with the calcinations treatment, which results the formation of mesoprous silica shell with hollow interiors. Significantly, the spherical shape is preserved for this hollow mesoporous silica spheres (HMMS) (Fig. 1C). As revealed by SEM image, a number of spheres have a hole on the surface, indicating the hollow structures (Fig. 1C). TEM images further confirm that the HMMS gives the hollow interiors approximate 600 nm, originated from the carbon sphere core and mesoporous silica shell about 120 – 150 nm (Fig. 2C and 2D). That is the regular stripe-like mesochannels encircle the cavity.

A wide weak peak still appears at $2\theta = 0.90^{o}$ for small-angle XRD pattern, suggesting the retained of mesoporous structure (Fig. 1D). It should be noted that the diffraction peak shifted to the higher angle region (from $2\theta = 0.86$ to 0.90^{o}), implying a certain extent shrinkage of the mesoporous silica shell. N_2 adsorption/desorption isotherms of HMSS shows a representative typical type-IV curve consisting with the H1-type hysteresis loop in high relative pressure (p/p_0) range of 0.5 - 0.7, indicating the existence of large mesopore. The surface area and pore size distribution of HMSS are 326.5 $m^2 g^{-1}$ and 6.0 nm, which is slightly lower than that of CS@SBA-15 (Table 1). The increased pore volume (0.42 $cm^3 g^{-1}$) derives from the hollow interiors of HMSS.

To explore the role of $MgSO_4$ in the coating process, the CS@SBA-15 100H sample is synthesized without addition of $MgSO_4$. It is found that the CS@SBA-15 100H sample still possesses the spherical morphology with the diameter about 900 nm, indicating the mesoporous silica coated on the surface of carbon spheres (Fig. 4A). However, some sticky particles with irregularly rounded shapes are observed on the surface of spheres, resulting the rough surface and nonuniform coating. The obtained HMSS 100H after removal of carbon sphere core under air atmosphere is maintained

Comment [HL9]: ‘ununiform’

the hollow structure (Fig. 4B). Furthermore, the CS@SBA-15 100H core-shell structure and HMSS 100H hollow sphere present a type IV isotherm (Fig. S1), the BET surface area, pore size and pore volume are 376.1 $m^2 g^{-1}$, 6.3 nm, 0.31 $cm^3 g^{-1}$ and 239.9 $m^2 g^{-1}$, 6.1 nm, 0.37 $cm^3 g^{-1}$, respectively (Table 1), which are all lower than that corresponding to samples with addition of $MgSO_4$. Furthermore, the XRD patterns of core-shell structures and hollow spheres both display a distinct diffraction peak (Fig. S2). These results disclose that the introducing of inorganic salt $MgSO_4$ can realize the uniform coating of mesoporous silica due to the enhanced electrostatic interaction between triblock copolymer surfactant and silica precursor.[24,26]

For the traditional synthesis approach of SBA-15, the pore size distribution is sensitive with the hydrothermal temperature. Generally, higher hydrothermal temperature treatment is in favor of larger pore size distribution.[42] Therefore, in order to obtain large pore size mesoporous silica shell during the coating process, an elevated hydrothermal temperature is chosen at 130 °C. It is noticeable that the carbon spheres are coated by mesoporous silica shell (CS@SBA-15 130H-$MgSO_4$) at such high hydrothermal temperature with the average size of 900 nm. From the broken spheres, the core-shell structure is apparently observed (Fig. 4C). The hollow spheres (HMSS 130H-$MgSO_4$) are clear appeared after removal the carbon core (Fig. 4D), further demonstrating the successful coating after high hydrothermal treatment. Furthermore, N_2 adsorption/desorption isotherms of CS@SBA-15 130H-$MgSO_4$ and HMSS 130H-$MgSO_4$ exhibit typical IV curves with condensation steps at high relative pressure (P/P_o) of 0.7-0.8, indicating the larger pore size distribution (Fig. S1). As shown in Table 1, the pore size distributions center at ~ 8.4 and 8.2 nm, respectively.

Comment [HL10]: 'removing the carbon core'

Base on the aforementioned results, mesoporous silica SBA-15 can be coated on the surface of carbon spheres under a low concentration of triblock copolymer and strong acidic system at room temperature. The hydrogen ion interacts with the oxygen derived from the hydrophilic chain of block copolymer, and then reacts with the silica precursor through electrostatic interaction (Scheme 1).[43] The micelles assemble to intermediate mesostructures, thus subsequent adsorb on the surface of carbon spheres

via polar interactions and hydrogen bonding. Because the abundant OH and C=O groups exist on the surface of carbon spheres and present hydrophilic property, which is confirmed by FTIR (Fig. S3). Moreover, the carbon spheres also can interact with cation surfactant hexadecyltrimethylammonium bromide (CTAB) and fabricate the hollow mesoporous silica spheres with small pore size (~ 2.0 nm) distribution (Fig. S4). This phenomena further verify that abundant OH and C=O groups around the surface of carbon sphere facilitates the coating of mesoporous silica, even in acidic system.

4. Conclusions

In summary, we have demonstrated a direct triblock-copolymer-templating strategy to prepare carbon sphere@mesoporous silica core-shell structures and mesoporous silica hollow spheres with controllable large mesopores *via* using P123 as surfactant template and TEOS as silica source in an acidic medium. The large mesopore can be well realized from 6.3 to 8.4 nm by changing the hydrothermal temperature and ionic strength. This elegant design with carbon spheres as core and large pore mesoporous silica as the shell renders fascinating features and advantages. First, these large pores CS@SBA-15 and HMSS possess diversified applications on adsorption, drug-release and catalyst carrier. Second, carbon spheres as a benign and hydrophilic surface can offer a site for adsorption of metal ions and organic molecules to construct other functionalized core-shell and hollow structures. Third, the carbon spheres are easily coated on the surface of other nanocrystals and protected the cores, which is beneficial for the further formation of multilayer large pore mesoporous silica encapsulating core-shell and yolk-shell structures. At last, these large mesopore channels afford location for loading and nanocasting template for other mesoporous shells. Therefore, for fundamental interest and methodology outlook, the current work not limits on synthesis of mesoporous silica hollow spheres with large pore size, as well as provides the extensive directions for synthesis other large pore mesoporous core-shell, yolk-shell and hollow structures.

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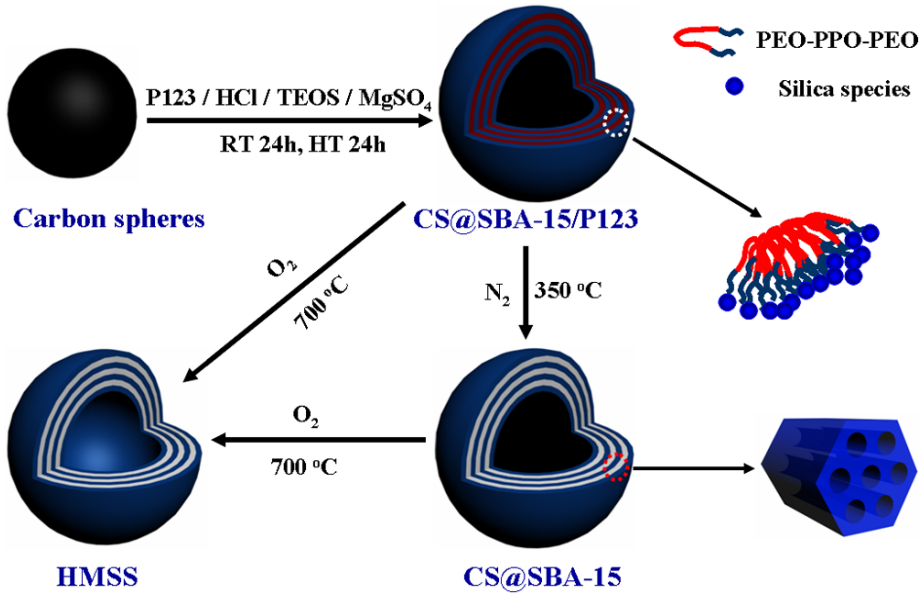

Scheme 1. Preparation procedure for the large mesopore coated carbon sphere core-shell structure (CS@SBA-15) and the corresponding hollow mesoporous silica spheres (HMSS).

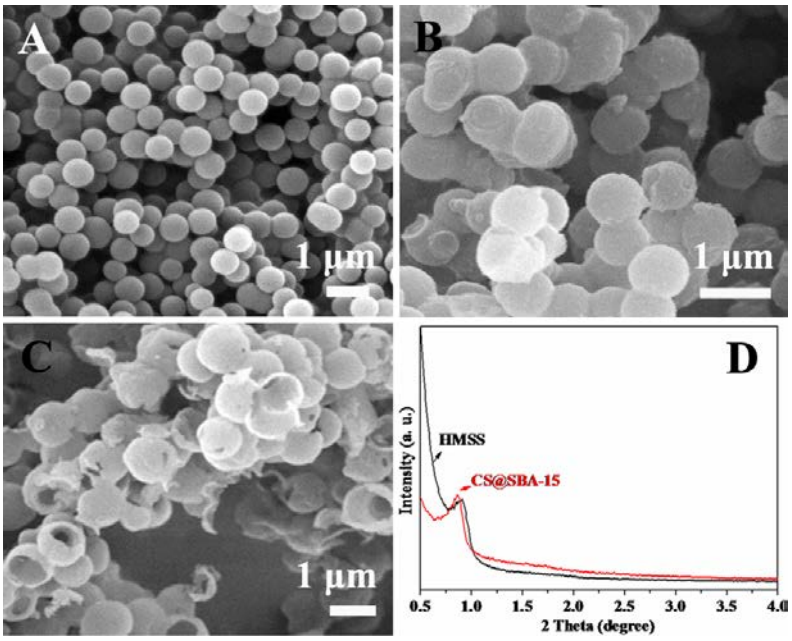

Fig. 1 SEM images of (A) carbon spheres prepared through a hydrothermal method by using glucose as the carbon species, (B) large mesopore silica coated carbon spheres (CS@SBA-15) core-shell structures prepared by using carbon spheres as a core, Pluronic P123 as the surfactant template, TEOS as the silica source, anhydrous magnesium sulfate as the inorganic salt in HCl solution with hydrothermal treatment at 100 °C for 24 h and calcination at 350 °C for 5 h under nitrogen atmospheres, (C) hollow mesoporous silica spheres (HMSS) after calcination at 700 °C for 3h under air atmosphere, (D) small-angle X-ray diffraction pattern of CS@SBA-15 and HMSS.

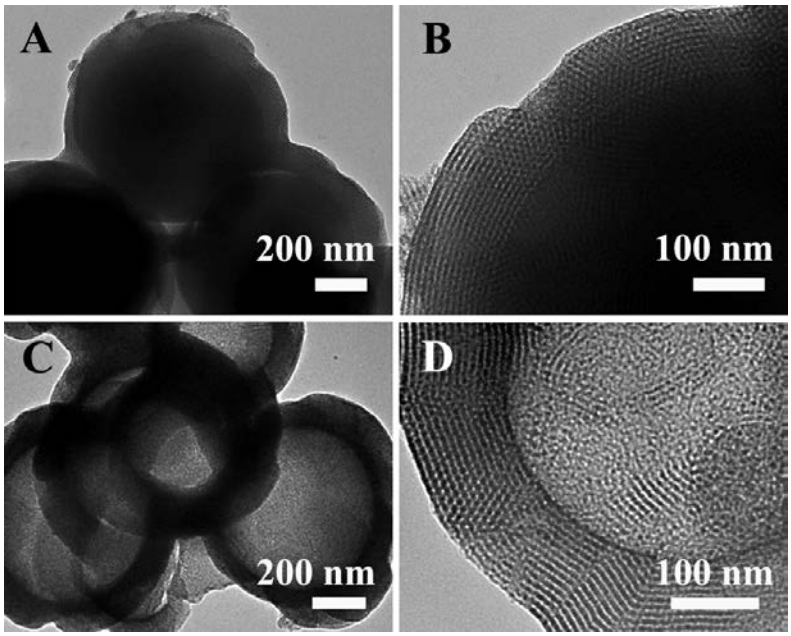

Fig. 2 TEM images of (A) and (B) CS@SBA-15 core-shell structures after calcination at 350 °C for 5 h under nitrogen atmosphere; (C) and (D) HMSS after calcination at 700 °C for 3 h under air atmosphere.

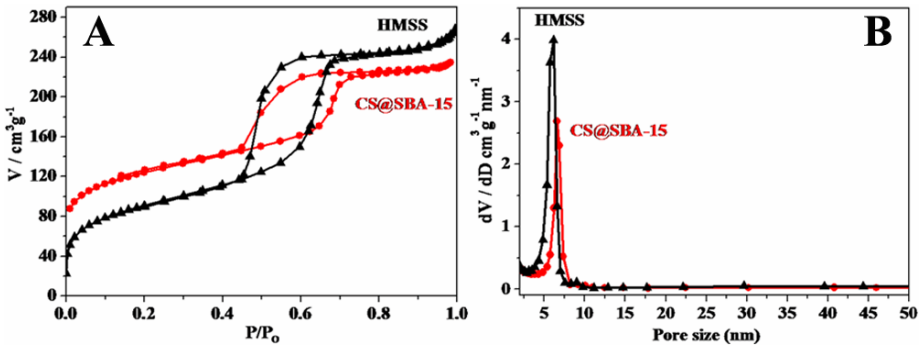

Fig. 3 (A) N_2 sorption isotherm curves and (B) pore size distribution plots of CS@SBA-15 and HMMS.

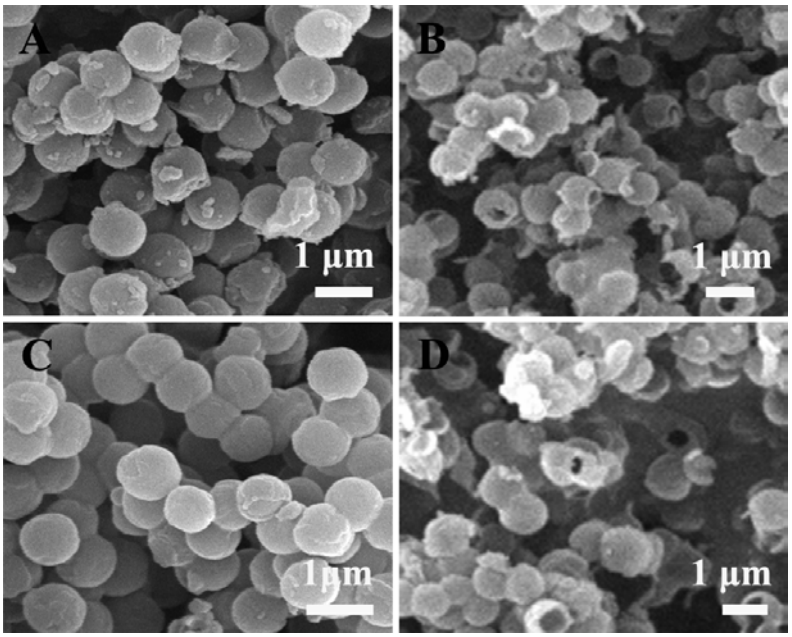

Fig. 4 SEM images of (A) CS@SBA-15 100H, without addition of anhydrous magnesium sulfate and hydrothermal treatment at 100 °C; (B) the corresponding hollow mesoporous silica spheres (HMSS 100H) after calcination at 700 °C for 3 h under air atmosphere. (C) CS@SBA-15 130H-$MgSO_4$, with the anhydrous magnesium sulfate as inorganic salt and hydrothermal treatment at 130 °C; and (D) the hollow mesoporous silica spheres (HMSS 130H-$MgSO_4$).

Table 1. Physicochemical properties of CS@SBA-15 and HMSS.

Sample	S_{BET} (m^2g^{-1})	Pore size (nm)	V_t (cm^3g^{-1})
CS@SBA-15	438.4	6.7	0.36
CS@SBA-15 100H	376.1	6.3	0.31
CS@SBA-15 130H-$MgSO_4$	318.1	8.4	0.33
HMSS	326.5	6.0	0.42
HMSS 100H	239.9	6.1	0.37
HMSS 130H-$MgSO_4$	277.7	8.2	0.62